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(54) Powder coating compositions

(57) A powder coating composition comprises a dry particulate mixture of (1) a thermosetting or thermoplastic resin and (2) vesiculated polymer granules having a volume mean diameter of 3 to 30 microns and formed of a polymeric material which is not melted or degraded during any of the conditions of time and temperature which arise during preparation or use of the compositions. The amount of the polymer granules in the composition is at least 40% by volume. The powder coating compositions produce a matt finish rather than the previous glossy style. The polymeric granules preferably are spherical and the vesicles occupy from 5 to 95% of the volume of the granules. The powder compositions can be used for wide variety of uses.

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This invention relates to resinous compositions and particularly to powder coating compositions.

Powder coating compositions are being used in increasing amounts and in an increasing number of applications. They have major advantages but
5 due to their methods of application the coatings produced tend to be glossy rather than of a matt finish. There is a desirability to obtain matt finishes.

According to the present invention a powder coating composition comprises a substantially dry particulate mixture of a thermosetting resin or of a thermoplastic resin and vesiculated polymer granules having a volume
10 mean diameter of from 3 to 30 microns and formed of a polymer material that is not melted or not substantially degraded respectively under any conditions of temperature and time required to prepare said composition and also to cure said thermosetting resin composition and under any conditions of temperature and time required for the application of said
15 thermoplastic resin composition to a substrate and the amount of the polymer granules being less than 40% by volume of said mixture.

The powder coating compositions of the present invention are based on a resin which will be either a thermosetting resin or a thermoplastic resin but compositions based on thermosetting resins are preferred.
20 Thermosetting resins are those which when cured, usually through the action of a curing agent, do not melt or otherwise soften on heating.

Generally speaking typical thermosetting resins are epoxy resins, polyurethanes, polyester resins, epoxy-polyester hybrid resins and acrylic resins. Epoxy resins are available which cure through the action of a curing
25 agent at various rates depending also on the curing temperature. Compositions which melt, fuse and cure in 60 seconds or less are obtainable.

Typically curing agents based on dicyandiamide can be used particularly the modified and substituted types.

Polyester resins such as saturated oil-free resins based on isophthalic or terephthalic acids reacted with diols to produce hydroxyl-terminated resins can be used. Such resins can be cured by reaction with an amino resin e.g. melamine-formaldehyde resin. Polyester resins with free hydroxyl groups can be cured with isocyanates, such as isophorone diisocyanate which is blocked with a blocking agent, e.g. caprolactam. Such cured resins contain urethane groups and, strictly speaking, are polyurethanes. Other polyesters containing carboxyl groups can be used and these can be cured using polyepoxides, e.g. triglycidyl isocyanurate.

Polyester-hybrids can be used as thermosetting resins and can be the reaction product of an epoxy resin and a polyester.

Thermosetting acrylic resins such as those obtained by polymerising a methacrylate on to an acrylic backbone can be used. Dibasic acids can be used for cross-linking or curing the resin. Other suitable curing agents are carboxy-terminated polymers.

Thermoplastic resins which can be used to form the powder coating composition of the present invention are polyvinyl polymers, polyamides, thermoplastic polyesters, polyolefines and cellulosics. Typical resins are the plasticized polyvinyl chlorides, polyamides having suitable melting temperatures, polyethylene, polypropylene, resins of cellulose acetate butyrate, polyesters based on terephthalic acid and 1,4-butanediol, ethylene chlorotrifluoro-ethylene polymers, poly(vinylidene fluoride) and poly(phenylene sulphide).

Generally speaking the powder coating compositions of the present invention will, in the case of a thermosetting resin composition, usually also contain a curing agent for the resin (as described hereinbefore), a flow additive and the vesiculated polymeric granules. In the case of a powder
5 coating composition based on a thermoplastic resin then the composition will usually also contain a plasticizer, a stabiliser and the vesiculated polymer granules.

The resin composition can contain pigments such as titanium dioxide and coloured pigments and dyes as is necessary or desirable. Titanium
10 dioxide coloured dyes and/or coloured pigments can be present in the composition inside the vesiculated polymer granules or exterior thereof.

The granules of a polymer material contain one or more vesicles the walls of which vesicles are provided by the polymer. Preferably the granules are substantially spherical and the vesicles occupy from 5% to 95% of the
15 total volume of the granules. Most preferably the vesicles occupy from 20% to 80% of the volume of the granules.

The granules have a size such that the volume mean diameter is from 3 to 30 microns and preferably from 5 to 20 microns.

Typically the vesicles in the preferred granules will be substantially
20 spherical in shape and have a diameter less than 20 microns and preferably from 0.1 to 7 microns, most preferably 0.1 to 1 micron.

Generally speaking the nature of the polymer of the granules is not critical and can be a polyester, obtained by condensation of a polycarboxylic acid and a polyol, a polyester amide, a polyurethane, a urea-aldehyde resin, a
25 cellulosic ester or any other suitable material. Preferably the polymer is an unsaturated polyester resin cross-linked with an unsaturated monomer.

Whilst the granules can be formed from a wide variety of different polymers, however, the polymer should be one that is not melted, or not substantially degraded, in the case of a thermosetting resin composition, under the conditions of temperature and time of mixing or preparing the composition and later curing and, in the case of a thermoplastic composition, under the conditions of temperature and time for the application of the composition to a substrate.

Other types of polymer particles which may be used in the present invention are those known as water-insoluble core-sheath polymer particles and particularly those having a single vesicle per particle. In such particles the core is formed of polymeric material which will swell on contact with an appropriate substance and the sheath is formed of another polymeric material which is permeable to the substance required to react with the core.

The polymeric granules, if desired, can contain a pigment such as titanium dioxide pigment which can be present in the vesicles, or in the polymeric material or in both.

The granules can be formed by any suitable method but usually will involve the formation of a water-in-oil emulsion of a polymeric material, such as a polyester resin dissolved in an oil material e.g. styrene or a cross-linking monomer. This emulsion is then dispersed in a further aqueous phase. Polymerisation produces an aqueous dispersion of polymer granules having vesicles.

The aqueous dispersion of polymer granules prepared by the preferred process can be dried by the process as described in patent specification No. GB 2 205 154A and the dried composition then used to manufacture the powder coating composition. In the process described and

claimed in specification GB 2 205 154A the aqueous dispersion is dried by heating in a non-oxygen containing atmosphere under such conditions of time and temperature that substantial deterioration of said particles is minimised.

5 When the polymer granules contain a pigment then the amount of the pigment can be from 1% to 60% by weight of the weight of the granules, preferably from 5% by weight to 45% by weight.

 The amount of the polymer granules in the powder coating composition can vary over a wide range but should be less than 40% by
10 volume of the composition and preferably from 5% to 30% by volume.

 Generally speaking there are two main methods for the manufacture of powder coating compositions; namely a melt-mixing process or a dry-blending process.

 In a melt mixing process the resin, the vesiculated polymer granules
15 and any other agents are mixed together in a dry form and then heated while undergoing mixing or extrusion prior to cooling. The heating should be sufficient to melt the resin in the mixture but not the granules and also the temperature and time is not sufficient to introduce unacceptable premature curing of a thermosetting resin composition. The extruded or otherwise
20 mixed composition is cooled and granulated and milled to a desired final particle size. If desired any desired final additives can be introduced into the composition prior to packaging.

 In a dry blending process the resin in finely divided form is mixed with the vesiculated polymer granules and any other desired ingredients and
25 mixed together in a high intensity mixer. The mixed composition is cooled and any desired post blending additions made. If desired the mixed

composition may be classified to remove undesired oversized or undersized particles prior to packing.

5 The powder coating compositions of the present invention can be used for a wide variety of purposes and applied by any of the widely used techniques such as electrostatic spray coating, fluid bed coating, electrostatic fluid bed coating and hot flocking. Electrostatic spray coating is the preferred manner of application.

10 It will be appreciated that the powder coating compositions of the present invention are substantially dry particulate mixtures and are substantially free of solvents or dispersion media.

Coated products are produced having a matt finish with an even non-blotchy appearance. Prior to the use of vesiculated polymer granules matt finished products have not possessed the necessary appearance and some have had an uneven blotchy finish.

15 The products of the present invention find use for coating a wide range of products to be used indoors and outdoors.

The invention is illustrated in the following Examples in which all parts are by weight.

EXAMPLE 1 (Production of Beads)

20 An unsaturated polyester resin was prepared by condensing together maleic anhydride, phthalic anhydride and propylene glycol in the molar ratio 3:1:4.5. The product had an acid value of 16 mg KOH per gram of solid resin.

25 Into 44 parts of a 57% weight solids solution of the above resin in styrene was milled 3.5 parts of titanium dioxide pigment obtainable under the name TIOXIDE R-HD6 and 0.18 parts of magnesium oxide, until they were

thoroughly dispersed (about 30 minutes). To this mixture was added 20 parts of styrene and 4.9 parts of hot water (around 80°C), and milling was continued for 1 minute. This oil phase was then left to stand for one hour.

5 Separately, 0.6 parts of a 90% weight solids aqueous solution of an ammonium nonylphenol ethoxylate sulphate surfactant were mixed with 0.18 parts of industrial methylated spirits and 0.42 parts of water. This was milled with 42 parts of water at 50°C, to give an aqueous phase, which was slowly added to the oil phase with stirring. The mixture formed was milled for 10 minutes to give a water-in-oil emulsion.

10 45.5 parts of this emulsion were immediately added to a further aqueous phase, containing 5 parts of a 7.5% weight solids solution of polyvinylalcohol (as stabiliser), 1 part of a 1.5% weight solids solution of hydroxyethyl cellulose thickener and 80 parts of water, and was milled for 3 minutes, at which point a water-in-oil-in-water system had formed, with the
15 oil globules averaging around 11 microns in diameter.

28 parts of hot water were then added, with minimum possible milling, followed by 0.006 parts of ferrous sulphate, dissolved in a small quantity of water, 0.1 parts of diethylenetriamine, also dissolved in a small quantity of water, and 0.156 parts of cumene hydroperoxide. The slurry was left
20 undisturbed overnight and exothermed to over 50°C, ensuring complete curing of the unsaturated polyester. This gave a 16.1% weight solids slurry of cross-linked vesiculated pigmented polyester resin beads.

This slurry was dried by the method described and claimed in patent application GB 2 205 154A, as follows. To 4000 parts of slurry were added
25 15 parts of 10% ammonia solution and 40 parts of a 5% solution of the flocculating agent. This flocculating agent is the mono-acetate salt of a

diamine derived from a fatty acid. The slurry was then heated to 70°C and stirred until flocculation occurred. The batch was filtered through a conventional vacuum filter, and was washed with clean water until no further poly(vinyl alcohol) could be detected in the filtrate. Testing for poly(vinyl alcohol) consisted of mixing a sample of the filtrate with ten times its volume of acetone, whereupon any poly(vinyl alcohol) present is precipitated as a white turbidity. The resulting filter cake contained 18.4% by weight of beads solids.

2 kg of filter cake was broken up and placed on a tray in an oven equipped with a thermostat and able to be flushed through with nitrogen gas. The cake was then heated to 110°C in an atmosphere of nitrogen for 16 hours, after which time no further weight loss could be detected.

The dried beads formed a soft, friable white mass, which could be brushed through a sieve of aperture 106 microns without leaving a residue.

Example 2 (Standard)

A conventional powder coating with a pvc (pigment volume concentration) of 15% was made by the following method. 692 parts of prechipped epoxy resin (Dow 663U), 102 parts chipped flow control masterbatch (5% by weight Modaflow flow control agent (a copolymer of ethyl acrylate and 2-ethylhexyl acrylate) in Dow 663U epoxy resin), 40 parts curing agent being an accelerated dicyandiamide (Dow DEH 41) and 500 parts titanium dioxide pigment sold under the name TIOXIDE TR92 were blended in a water-cooled Henschel mixer. The blending was carried out at a rotor speed of 1800 rpm for five minutes. The sides and rotor of the machine were scraped down after the initial three minutes milling.

The resulting premix was extruded using a PR46 Buss Ko-Kneader, running at slow speed, at 100°C, then was cooled and chipped in a small rotating knife Cumberland granulator. The chipped extrudate was then ground in a mini-KEK pin-disc mill, and the powder produced was passed
5 through a 200 mesh sieve to remove any particles above 75 microns before spraying.

The powder was applied, using a manual Volstatic electrostatic spray unit with the voltage regulated to 90 kV negative, onto Bonderite DG12 (iron phosphate) panels. The powder was fused and cured to a continuous
10 coat by stoving the panels at 180°C for 10 minutes. A Permascope, Type ES, was used to measure the coating thickness; panels were selected with a cured coating thickness of between 45 and 55 microns.

Colour measurements were made on the panels using a Gardner XL-23 colorimeter. L and b values were measured on the CIE Lab scale. Glosses
15 were measured using a Byk-Labotron Multigloss glossmeter.

Examples 3-6 (Invention)

A series of powder coatings was made, containing the dry vesiculated pigmented polymer beads made in Example 1. The pigment volume concentration was maintained at 15%, and the bead volume concentration
20 (bvc) was varied between 10% and 40%. The powder coatings were made by the same method as was used in Example 2, with the beads added at the same stage as the pigment. The quantities used, in parts by weight, were as follows:

	Example	3	4	5	6
	pvc	15%	15%	15%	15%
	bvc	10%	20%	30%	40%
	Epoxy resin	613	531	449	367
5	Flow control masterbatch	90	78	66	54
	Curing agent	35	30	26	21
	TiO ₂ pigment	500	500	500	500
	Beads	30.4	60.7	91.4	121.4

Testing was carried out as in Example 2. The results are tabulated below.

10 Example 7 (Comparator)

A further powder coating was made up, with an inorganic extender (calcium carbonate, Durcal 5), of substantially the same size as the beads, used in their place. The pigment volume concentration was maintained at 15%, and an extender volume concentration (evc) of 20% was used. The powder coating was made by the same method as was used in Example 2. The quantities used, in parts by weight, were as follows:

	Example	7
	pvc	15%
	evc	20%
20	Epoxy resin	531
	Flow control masterbatch	78
	Curing agent	30
	TiO ₂ pigment	500
	Extender	443

Testing was carried out as in Example 2. The results are tabulated below.

Results of Examples 2-7

Example	pvc	bvc	evc	L	b	20 ⁰ gloss	60 ⁰ gloss
2	15%	-	-	94.8	0.4	77	98
3	15%	10%	-	94.9	1.7	32	63
4	15%	20%	-	94.9	2.9	9	32
5	15%	30%	-	94.9	3.6	2	8
6	15%	40%	-	92.0	6.4	1	2
7	15%	-	20%	93.6	0.6	29	75

- Example 6, with 40% bvc, had not fused into a continuous coating, and was not a usable system, therefore. Example 7, with 20% evc, had a substantially lower brightness than the standard, Example 2, or than the powder coating with an equivalent volume of beads, Example 4. Its gloss was far higher than that in Example 4, also, the beads evidently being the superior matting agent.
- The increase in b value (i.e yellow tint) with increasing bvc was not due to thermal degradation of the beads, as a sample of beads heated under the same conditions showed very little change in colour. It is believed that the particular curing agent used in these examples (Dow DEH41) is an amine. Amines in general are known to interact with polyesters on heating to produce yellowish or brownish products.

Example 8 (Standard)

- A conventional powder coating with a pvc of 15% was made by the following method. 691 parts of prechipped polyester resin (Uralac P2400, from DSM Resins), 58 parts triglycidyl isocyanurate (TGIC, Araldite PT810, from Ciba-Geigy), 93 parts chipped flow modifier (Urad P2518, from DSM Resins), and 500 parts of a general purpose titanium dioxide pigment sold

under the name TIOXIDE TR92 were blended in a water-cooled Henschel mixer. The blending was carried out at a rotor speed of 1800 rpm for five minutes. The sides and rotor of the machine were scraped down after an initial three minutes milling period.

5 The resulting premix was extruded using an extruder (PR46 Buss Ko-Kneader), running at slow speed, at 100°C, then was cooled and chipped in a small rotating knife Cumberland granulator. The chipped extrudate was then ground in a pin-disc mill (mini-KEK), and the powder produced was passed through a 200 mesh sieve to remove any particles above 75 microns before
10 spraying.

 The powder was applied, using a manual electrostatic spray unit (Volstatic) with the voltage regulated to 90 kV negative, on to iron phosphate panels (Bonderite DG 12). The powder was fused and cured to a continuous coating by stoving the panels at 200°C for 10 minutes. A
15 Permascope, Type ES, was used to measure the coating thickness, panels were selected with a cured coating thickness of between 45 and 55 microns.

 Colour measurements were made on the panels using Gardner XL-23 colorimeter. L and b values were measured on the CIE Lab scale. Glosses were measured using a Byk-Labotron Multigloss glossmeter.

20 Examples 9-10 (Invention)

 Two powder coatings were made, containing the dry vesiculated pigmented polymer beads made in Example 1. The pigment volume concentration was maintained at 15%, and the bead volume concentration (bvc) was set at 10% and 20%. The powder coatings were made by the same
25 method as was used in Example 8, with the beads added at the same stage as the pigment. The quantities used, in parts by weight, were as follows:

	Example	9	10
	pvc	15%	15%
	bvc	10%	20%
	Polyester resin	615	533
5	TGIC	52	45
	Flow modifier	83	72
	TiO ₂ pigment	500	500
	Beads	30.8	61.6

10 The testing was carried out as in Example 8. The results are tabulated below.

Example 11 (Comparator)

A further powder coating was made-up, with an inorganic extender (calcium carbonate, Darcac 5), of substantially the same size as the beads, used in their place. The pigment volume concentration was maintained at 15%, and an extender volume concentration (evc) of 20% was used. The powder coating was made by the same method as was used in Example 8. The quantities used in parts by weight, were as follows:

	Example	11
	pvc	15%
20	evc	20%
	Polyester resin	533
	TGIC	45
	Flow modifier	72
	TiO ₂ pigment	500
25	Extender	450

Testing was carried out as in Example 8. The results are tabulated below.

Examples 12-13 (Invention; dry blending)

Further powder coatings were made up at intermediate bead volume concentrations, by the blending of equal volumes of two powder coating powders at different bvcs, to give a product of effective bvc equal to the mean of the individual bvcs. As a check, a blend was made of the 20% bvc system and the 0% bvc (standard) system, giving an effective bvc of 10%. This performed identically to the powder coating made ab initio at 10% bvc. Therefore, the blends of 0% bvc and 10% bvc powders (giving an effective bvc of 5%) and of 10% bvc and 20% bvc powders (giving an effective bvc of 15%) were considered to be equivalent to powder coatings made ab initio at 5% bvc and 15% bvc respectively. The powders were applied and tested as in Example 8. The results are tabulated below.

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Results of Examples 8-13

Example	pvc	bvc	evc	L	b	20° gloss	60° gloss
8	15%	-	-	96.1	0.3	87	97
12	15%	5%	-	96.4	0.6	48	74
9	15%	10%	-	96.3	0.8	24	51
13	15%	15%	-	96.4	0.9	8	27
10	15%	20%	-	96.4	1.1	2	9
11	15%	-	20%	94.6	0.3	18	60

Example 11, with 20% evc, had a substantially lower brightness than the standard, Example 8, or than the powder coating with an equivalent volume of beads, Example 10. Its gloss was far higher than that in Example 10, also, the beads evidently being the superior matting agent. The increase

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in b value (i.e. yellow tint) with increasing bvc was far lower than for the corresponding epoxy system, Example 2-6, and would not constitute a significant drawback in use. It is noteworthy that when a graph of the 60° gloss against the bvc was plotted for Examples 8, 9, 10, 12 and 13, there was a
5 linear relationship between the two variables. The majority of matting agents have a far less straightforward effect on gloss. Thus, these beads will make it far easier to select a bvc to give a required 60° gloss result.

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CLAIMS

1. A powder coating composition comprising a substantially dry particulate mixture of a thermosetting resin or of a thermoplastic resin and vesiculated polymer granules having a volume mean diameter of from 3 to 30
5 microns and formed of a polymer material that is not melted or not substantially degraded respectively under any conditions of temperature and time required to prepare said composition and also to cure said thermosetting resin composition and under any conditions of temperature and time required for the application of said thermoplastic resin composition
10 to a substrate and the amount of the polymer granules being less than 40% by volume of said mixture.
2. A composition according to claim 1 in which the granules have a volume mean diameter of from 5 to 20 microns.
3. A composition according to claim 1 or 2 in which the granules have
15 vesicles which are substantially spherical in shape.
4. A composition according to claim 3 in which the vesicles have a diameter less than 20 microns.
5. A composition according to claim 4 in which the vesicles have a diameter of from 0.1 to 7 microns.
- 20 6. A composition according to claim 5 in which the vesicles have a diameter of from 0.1 to 1 micron.
7. A composition according to any one of the preceding claims in which the granules are substantially spherical.
8. A composition according to any one of the preceding claims in which
25 said granules contain vesicles occupying from 5% to 95% of the total volume of the granules.

9. A composition according to claim 8 in which said vesicles occupy from 20% to 80% of the volume of the granules.
10. A composition according to any one of the preceding claims in which the amount of the granules is from 5% to 30% of the volume of the mixture.
- 5 11. A composition according to any one of the preceding claims in which the thermosetting resin is an epoxy resin, a polyurethane, a polyester resin, an epoxy-polyester hybrid resin or an acrylic resin.
12. A composition according to any one of claims 1 to 10 in which the thermoplastic resin is a polyvinyl polymer, a polyamide, a thermoplastic polyester, a polyolefine or a cellulosic polymer.
- 10 13. A composition according to claim 11 in which a curing agent for said resin is present.
14. A composition according to claim 12 in which the mixture contains a plasticizer for the polymer.
- 15 15. A composition according to any one of the preceding claims in which titanium dioxide pigment is also present in the mixture.
16. A composition according to claim 15 in which the titanium dioxide is present in said granules.
17. A composition according to claim 16 in which the amount of titanium dioxide in said granules is from 1% to 60% by weight of said granules.
- 20 18. A composition according to claim 17 in which the amount is from 5% to 45% by weight.
19. A composition according to any one of the preceding claims in which the polymer granules are formed from a polyester, a polyester amide, a polyurethane, a urea-aldehyde resin or a cellulosic ester.
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20. A composition according to claim 19 in which the polymer granules are formed from an unsaturated polyester resin cross-linked with an unsaturated monomer.
21. A composition according to any one of the preceding claims in which
5 the polymer granules are core-sheath polymer particles.
22. A composition according to claim 22 in which each granule has a single vesicle.
23. A process for the manufacture of a powder coating composition which comprises mixing a thermosetting resin or of a thermoplastic resin and
10 vesiculated polymer granules having a volume mean diameter of from 3 to 30 microns and formed of a polymer material that is not melted or not substantially degraded respectively under the conditions of temperature and time of mixing and those required to cure said thermosetting resin composition and under the conditions of temperature and time for the
15 application subsequently of said thermoplastic resin composition to a substrate and the amount of the polymer granules being less than 40% by volume of said mixture.
24. A process according to claim 23 in which the mixture is heated to melt the resin and the mixture is extruded and cooled prior to grinding to the
20 desired final size.
25. A process according to claim 23 substantially as described in the foregoing Examples.
26. A powder coating composition when obtained by the process of any one of claims 23 to 25.

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